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Crystallization in the Na_2O–CaO–Al_2O_3–SiO_2–(LiF) glass compositions

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Abstract

Spodumene-nepheline glass-ceramics was prepared from Na_2O–CaO–Al_2O_3–SiO_2 glass compositions. Addition of LiF changes the course of the reaction toward the formation of β-spodumene together with nepheline. The crystallization of β-spodumene strongly reduced the thermal expansion coefficient from 70, in the base sample, to 17, in that containing 6 wt.% LiF $\times 10^{-7}\,°C^{-1}$ (20–700 °C). Addition of 3 wt% LiF is considered the best as it reduces the expansion coefficient and enhances the microstructure uniformity. Higher content of LiF results in impairing the machinability as the content of β-spodumene tends to exceed 50%. Li^+ substitute Na^+ cations resulting in the formation of β-Spodumene ss. However, shift in the nepheline *d*-spacing lines with the appearance of some unidentified ones may reflect a state of solid solution formation. The presence of fluorine in such glass structure is found to promote the nepheline growth. The transformation temperature (T_g) and the softening temperature (T_s) were reduced as a result to the addition of LiF.

Keywords: C. Thermal expansion; D. Glass; Crystallization; DTA; XRD

1. Introduction

Nepheline is a naturally occurring mineral present in silica poor rocks. The nepheline containing ceramics proved to be reliable and suitable for the use in dental applications. As it is generally desirable that the dental glass ceramics have good strength, suitable thermal expansion and good appearance [1,2]. Their properties must be strictly controlled to match the characteristics of ceramics with metal to suit dental applications. The control over the properties of nepheline containing ceramics is very important to be used in the crown construction [2,3]. The control mainly depends on the properties of the developed phases. The modification of the thermal expansion coefficient to match that of the metal substrates and the microhardness to match that of the natural enamel is a very important factor for the suitability to crown construction [4,5].

On the other hand, β-spodumene containing glass-ceramics attract considerable commercial interest because of their lower thermal expansion, together with remarkable chemical resistance and good microhardness. Fluorine on the other hand plays an important role in crystallizing β-spodumene phase in the glass-ceramics and promoting the nucleation and growth by the ingression of F ions into the glass network to replace non-bridging oxygen ions [6–11].

The current paper deals with the crystallization of β-spodumene phase simultaneously with nepheline in the Na_2O–CaO–Al_2O_3–SiO_2–(LiF) glass-ceramics. The content of β-spodumene phase will be utilized to control the value of the expansion coefficient. In addition, the role of LiF on the thermal behaviour, phase composition and microstructure will be assessed.

2. Experimental

The present composition, was within the Na_2O–CaO–Al_2O_3–SiO_2 system, based on the midway formula between anorthite $CaAl_2Si_2O_8$ and nepheline $NaAlSiO_4$, however, such phase was called lisetite [12] of $Na_2CaAl_4Si_4O_{16}$ formula. The compositions of the starting glasses are shown in Table 1. The batches were prepared using sodium carbonate (Merck) and calcium carbonate (BDH-GPR England), while silica and alumina were

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Table 1
Chemical composition of glass batches

Glass code	Chemical composition (wt%)				
	SiO_2	Al_2O_3	CaO	Na_2O	LiF
GL0	42.66	36.19	9.95	11.20	0.00
GL3F	41.42	35.14	9.66	10.87	2.91
GL6F	40.25	34.15	9.39	10.57	5.65

added as quartz' sand and pure reagent alumina (BDH). LiF (Panreac Spain) was added as nucleating catalyst.

The calculated batches were mixed in a ball mill for 2 h. Glasses were prepared by fusion of the homogenized batches in platinum crucible at temperatures between 1300 and 1400 °C/2 h. The molten glasses were prepared by casting on stainless steel mould followed by annealing at 500 °C.

DTA analysis was conducted on Setaram Labsys^M instrument furnace at a rate of heating 10 °C/min. The test was carried out using glass powders with grains of 250–350 μm size. The prepared glasses were subjected to controlled crystallization through sequential heat-treatment at temperatures between 800 and 1000 °C. The crystallized glasses were subjected to XRD analysis using Philips PW 1380 Apparatus using Cu target and Ni-filter to follow the developed phases.

The Expansion behavior was studied using Linseis dilatometer (model L76/1250) with a heating rate of 5 °C/min. The softening points and the transformation temperatures will be predicted in the prepared glasses, also the thermal expansion coefficients were calculated for both the prepared glasses and the corresponding glass ceramics.

SEM observations were done for glass-ceramic fractured samples etched for 30 s by sinking in a mixture of 1% HF + 1% H_2NO_3, The etched samples were rinsed by distilled water, dried and then coated by a thin film of carbon. The analysis was carried out using apparatus model XL30, Philips operating at 25 kV.

3. Results

The results of DTA analysis are shown in Fig. 1. The DTA pattern of GL0 sample shows no clear pattern; where there is no peaks are recorded up to 1000 °C. Only a small kink refers to the nepheline nucleation occurring at 788 °C. In GL3F glass, the DTA pattern shows the appearance of an endothermic peak at 650 °C and a sharp exothermic peak 810 °C. The endothermic peak is related to the nucleation, while the exothermic peak is related to the crystallization of β-spodumene. The increase in LiF addition in GL6F glass up to 5.65 wt.% results in shifting the position of the endothermic and exothermic peaks to the temperature of 600 and 715 °C, respectively, while the nucleation and crystallization temperatures were reduced.

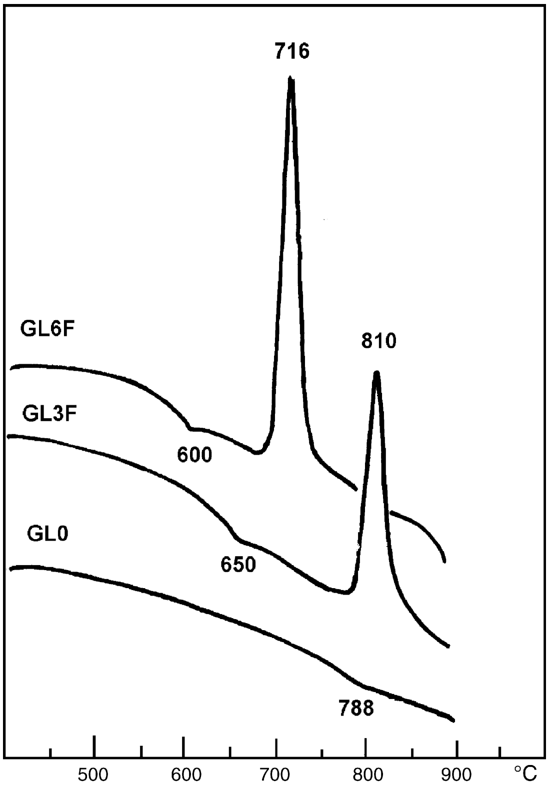


Fig. 1. DTA curves of GL0, GL3F and GL6F glasses.

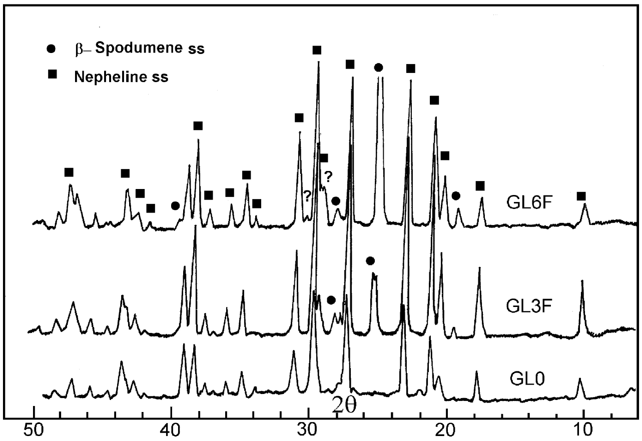
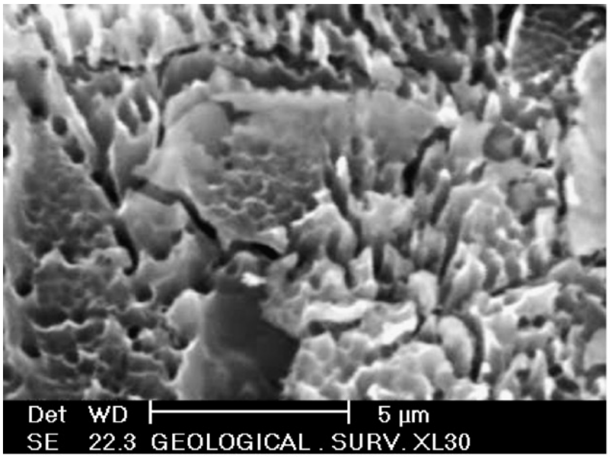


Fig. 2. XRD patterns of GL0, GL3F and GL6F glasses heat-treated at 800 °C/2 h + 900 °C/2 h.

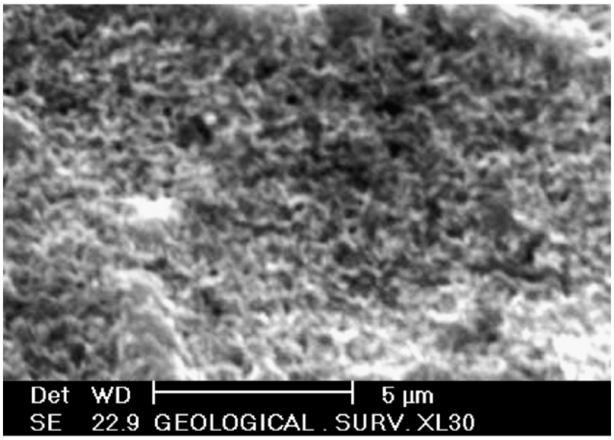
Table 2
Crystalline phases in the present glasses heat-treated at different temperatures

Glass no.	Heat treatment temperature (°C/2 h)	Developed phases
GL0	1. 800	Amorphous
	2. 1 + 900	Nepheline ss
	3. 2 + 1000	Nepheline ss
GL3F	1. 800	Nepheline ss + β-spodumene ss
	2. 1 + 900	Nepheline ss + β-spodumene ss
	3. 2 + 1000	Nepheline ss + β-spodumene ss
GL6F	1. 800	Nepheline ss + β-spodumene ss
	2. 1 + 900	Nepheline ss + β-spodumene ss
	3. 2 + 1000	Nepheline ss + β-spodumene ss

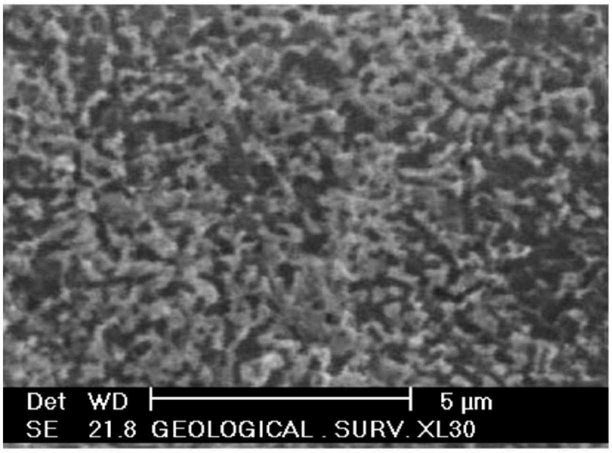
The results of XRD analysis of the different compositions are shown in Fig. 2 and Table 2. Nepheline is found to be the main crystalline phase in the base composition (GL0) of the prepared glass ceramics. On addition of LiF, the course of the



GL0



GL3F



GL6F

Fig. 3. SEM micrographs of the base and LiF-containing glass-ceramics obtained after heat-treatment of the glasses at 800 °C/2 h – 900 °C/2 h.

Table 3
The expansion behavior of the prepared glasses and the corresponding glass ceramics

Glass no.	Expansion behaviour				
	Glass			Glass-ceramics	
	T_g (°C)	T_s (°C)	CTE	Heat-treatment (°C/2 h)	CTE
GL0	706	740	73	800 + 900	70
GL3F	562	617	84	800 + 900	29
GL6F	522	563	92	800 + 900	17

CTE: coefficient of thermal expansion × 10^{-7} °C^{-1} (20–700 °C).

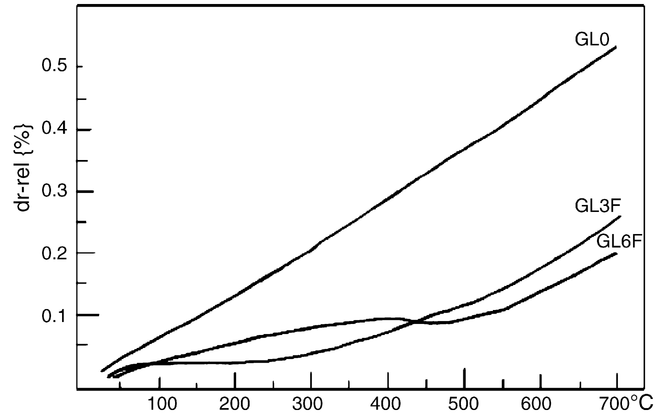


Fig. 4. Thermal expansion coefficient of the present glasses heat-treated at 800 °C/2 h + 900 °C/2 h.

reaction changes towards the crystallization of appreciable amount of β-spodumene together with the nepheline solid solution in GL3F and GL6F glasses. The amount of crystalline β-spodumene exceeds 30%, while nepheline is still the major phase. The shift in *d*-spacing lines of the developed nepheline to higher 2Θ angle, with appearances of some unidentified d-spacing lines at 3.20, 3.05, 2.95 Å may depict the possible solid solution of nepheline with incorporation of both Ca and Li in the nepheline structure.

The results of SEM are shown in Fig. 3. The base composition shows the appearance of nepheline intergrowths crystals embedded in the glassy phase. The grain size is about 3–5 µm. The microstructure is shown to develop freely uncontrolled which may deteriorate the mechanical properties. On the addition of LiF, fine granular grains of spodumene appear well distributed in the glassy phase. On the other hand, nepheline is shown to be rod like form crystals with very fine uniform habit. Finer grain size microstructure is achieved on heat-treatment at 800 °C/2 h + 900 °C/2 h and addition of 6% LiF.

The results of expansion behavior are shown in Table 3 and Fig. 4. The transformation temperature (T_g) and the dynamometric softening temperature of the glass were reduced with the addition of LiF. The expansion coefficient of the glass increases on the addition of LiF. On the other hand, the coefficient of thermal expansion was greatly reduced on the addition of LiF as a result to the crystallization of spodumene together with nepheline in the glass ceramics.

4. Discussion

It is well known that the manufacture of glass-ceramics involves three fundamental steps. The first is the melting of a glass-forming batch normally containing a nucleating agent. This melt is then cooled into a glassy body of a desired shape.

The glass body is then first heated to form nuclei of the proposed phases. The glass body is then heated to allow the growth of crystals. Thus, the glass body is initially heated to a temperature slightly above the transformation range to develop nuclei in the glass body. The nuclei provide sites for subsequent crystal growth. The crystallization mechanism leads to a substantially simultaneous growth of crystals on countless nuclei. Accordingly, porcelain conventionally consists of uniformly fine-grained crystals randomly oriented and homogeneously dispersed, throughout a residual glassy matrix.

As the target of the current paper is to study the crystallization of β-spodumene ss together with nepheline ss as a method to modify the thermal behaviour of the nepheline containing glass ceramics, so, the change of the course of the reaction toward the simultaneous crystallization of β-spodumene ss needs not only the substitution of Li^+ to Na^+ cation in the structure of nepheline, but also the presence of a mineralizer that enhances the crystallization of both phases. So, LiF is considered to be the best material, where fluorine is found to enhance the crystallization of β-spodumene and nepheline.

The crystallization of β-spodumene is found to modify the thermal expansion coefficients as shown in Fig. 4. So it becomes very easy to tailor the values of the expansion coefficients to suit the application in dental crown. On the other hand, it has been previously recorded that the crystallization of β-spodumene improves the microhardness values, until the content of β-spodumene exceeds 50%, then the increase in microhardness is then undesirable because of its effect on impairing the machinability.

In the current work, nepheline is found to crystallize lonely in GL0 glass but the crystallization seems to be uncontrolled. The effect of LiF addition is demonstrated on the different parameters. The course of the reaction changes toward the crystallization of β-spodumene beside the main crystalline nepheline phase. In addition, the nucleation and crystallization are shifted to lower temperatures on the increase of the content of LiF. Also the thermal expansion coefficient is found to be reduced as a result to the crystallization of the β-spodumene phase.

The developed β-spodumene phase tends to harden the body and thereby impair the machinability character according to their amount, growth and distribution in the glassy matrix. However, to achieve a much lower coefficient of expansion of less than $40 \times 10^{-7}\ {}^{\circ}C^{-1}$, β-spodumene solid solution should comprise at least about 25% of the total crystalline phases. Therefore, the proportion of β-spodumene solid solution must not be more than 50%, otherwise, the hardness will increase sharply and the glass ceramics will no longer be considered machinable [6].

The incorporation of LiF in the base glass greatly lowers the endothermic peak or the nucleation and crystallization temperatures. In addition, the fluorine-containing glasses not only exhibited sharp and intense exothermic peaks, but also reduce the temperature of glass melting. Nepheline and spodumene were the developed crystalline phase assemblages formed at 800–1000 °C in the glasses containing LiF. In addition to the shift of *d*-spacing that predicts the substitution of Li^+ to Na^+ in the nepheline resulting in the crystallization of the β-spodumene phase solid solution. Also, nepheline solid solution was mentioned by many authors, where Ca and Li can incorporate in its structure [13,14]. However, the pre-mentioned unidentified *d*-spacing lines (3.20, 3.05, 2.95 Å) and the shift of its values to higher 2Θ angle, may reflect such solid solution state.

The incorporation of fluorine in the silicate structure have great effects on crystal–liquid phase equilibrium and on viscosity, which are of interest in reducing the melting temperature, viscosity of glass and enhancing the crystallization Incorporation of fluorine in the glass structure results in the substitution of one Si–O–Si bond by two Si–F bonds [15,6]. The glass network is broken at Si–F, leading to the decrease of the viscosity, transformation temperature (T_g) of the glasses and higher CTE. In addition homogeneous microstructure is obtained in both GL3F and GL6F samples. The transition temperature (T_g) and the dilatometric softening point (T_s) of the glasses are shown in Table 3. The incorporation of LiF caused reduced T_g (°C) and T_s (°C) temperatures. In general, the glasses containing LiF have the lowest CTE values.

The prepared glass-ceramics have a complex matrix of physical properties, as they are chemically durable and resistant to withstand attack by food contact in addition to the low melting and good forming capabilities. The glass composition also crystallizes uniformly in situ to a fine-grained body exhibiting homogeneous properties. The presence of the CaO improved the melting and the expansion stability, while not substantially altering the physical properties of the final product.

The current work succeeded to prepare glass-ceramics containing β-spodumene-nepheline in solid solution with low thermal expansion while keeping a uniform microstructure. The crystallization of β-spodumene enhances the different properties and in addition it controls the uniformity of microstructure and reduces the chance for local nepheline intergrowth through the catalytic effect of fluorine on the nepheline crystallization.

5. Conclusion

1. Spodumene-nepheline glass ceramics was prepared from Na_2O–CaO–Al_2O_3–SiO_2 glass compositions.
2. The addition of LiF changes the course of the reaction toward the formation of β-spodumene together with nepheline and reduces the transformation temperature (T_g) and the softening temperature (T_s).
3. Li^+ substitute Na^+ cations resulting in the formation of β-spodumene ss.
4. Higher content of LiF results in impairing the machinability as the content of β-spodumene tends to exceed 50%.
5. The presence of fluorine in the present silicate structure is found to promote the nepheline growth.
6. The crystallization of β-spodumene strongly reduces the thermal expansion coefficient to less than $20 \times 10^{-7}\ {}^{\circ}C^{-1}$ (20–700 °C) and enhances the microstructure uniformity.

References

[1] M.-C. Wang, N.-C. Wu, M.-H. Hon, Preparation of nepheline glass-ceramics and their application as dental porcelain, Mater. Chem. Phys. 37 (1994) 370–375.

[2] D. Radovan, D. Vera, V. Predrag, M. Smilja, M. Slobodan, Structural characterization of pure Na-nephelines synthesized by zeolite conversion route, J. Phys. Chem. Solids 65 (2004) 1623–1633.

[3] L. Hong, H. Pavel, D.V. John, Q. Maoxu, S. Yali, E.S. Donald, Effects of Al_2O_3, B_2O_3, Na_2O, and SiO_2 on nepheline formation in borosilicate glasses: chemical and physical correlations, J. Non-Cryst. Solids 331 (2003) 202–216.

[4] E.M.A. Hamzawy, C. Leonelli, Crystallization, microstructure and expansivity of spodumene-nepheline glasses, Glastech Ber. Glass Sci. Technol. 77 (2004) 289–294.

[5] E.M. El-Meliegy, Machinable spodumene–fluorophlogopite glass ceramic, Ceram. Int. 30 (6) (2004) 1059–1065.

[6] A.M. Hu, K.M. Liang, F. Zhou, G.L. Wang, F. Peng, Phase transformations of Li_2O–Al_2O_3–SiO_2 glasses with CeO_2 addition, Ceram. Int. 31 (2005) 11–14.

[7] A.M. Hu, K.-M. Liang, F. Peng, G.L. Wang, H. Shao, Crystallization and microstructure changes in fluorine-containing Li_2O–Al_2O_3–SiO_2 glasses, Thermochim. Acta 413 (2004) 53–55.

[8] D.U. Tulyaganov, S. Agathopoulos, H.R. Fernandes, J.M.F. Ferreira, Synthesis of lithium aluminosilicate glass and glass-ceramics from spodumene material, Ceram. Int. 30 (2004) 1023–1030.

[9] W. Moo-Chin, W. Nan-Chung, Y. Sheng, W. Shaw-Bing, Morphology and microstructure in the sintering of β-spodumene precursor powders with TiO_2 additive, J. Eur. Ceram. Soc. 23 (2003) 437–443.

[10] W. Moo-Chin, Y. Sheng, W. Shaw-Bing, W. Nan-Chung, Sintering Li_2O–Al_2O_3–$4SiO_2$ precursor powders with ultrafine TiO_2 additives, Mater. Chem. Phys. 76 (2002) 162–170.

[11] P. Riello, P. Canton, N. Comelato, S. Polizzi, M. Verità, G. Fagherazzi, H. Hofmeister, S. Hopfe, Nucleation and crystallization behavior of glass-ceramic materials in the Li_2O–Al_2O_3–SiO_2 system of interest for their transparency properties, J. Non-Cryst. Solids 288 (2001) 127–139.

[12] D.C. Smith, S.A. Kechid, G. Rossi, On the occurrence of lisetite, $CaNa_2Al_4Si_4O_{16}$, in the system Ca–Na–Al–Si–O, Am. Mineral. 71 (1986) 1372–1377.

[13] K.T. Tait, E. Sokolova, F.C. Hawthorne, The crystal chemistry of nepheline, Can. Mineral. 41 (2003) 61–70.

[14] D.A. Duke, J.F. Mac Dowell, B.R. Karstetter, Crystallization and chemical strengthening of nepheline glass-ceramics, Am. Ceram. Soc. 50 (1967) 67–74.

[15] M.W. McMillan, Glass-ceramic, second ed., Academic Press, London, 1979.